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SINTERING OF CERAMIC FORMED USING ULTRASOUND

S. A. Shakhov[1]

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The sintering of heat-resistant ceramic based on beryllium oxide and formed by hot casting using intense ultrasound is studied. It is determined that the changes due to the homogenization of the material and with the destruction and growth of defects in particles intensify sintering and make it possible to lower the sintering temperature (50 – 150°C) and decrease shrinkage (10 – 20%).

Sintering is one of the final stages of obtaining ceramic materials. At this stage the process of consolidation of a disperse system is actually completed and the final formation of the structure and properties of the ceramic material occurs. A characteristic feature of the sintering of a ceramic consisting of pure oxides is that the process proceeds in the solid state. This makes it necessary to use highly disperse powders in the technological process. However, such powders do not press easily and are absolutely unsuitable for formation by hot casting.

One of the promising directions for intensifying the formation process is activation of disperse systems by ultrasound. Ultrasonic treatment produces a number of considerable changes in the structural state of powders [1]. Changes of this kind can affect the character of the flow of consolidation at the next stage of the technological process, i.e., during sintering. This dictated the direction and volume of research whose objective was to study the sintering of heat-resistance ceramic consisting of beryllium oxide, formed by hot casting with intense ultrasound.

The samples (7.8 mm in diameter and 20 mm high) for the investigations were cast in an ultrasonic apparatus for continuous casting BChM-UZ [2] with ultrasonic power from 0 to 4 kW. Slips prepared from beryllium oxide powder (BeO content — 99.84%, specific surface area — 1.57 m^2/g) and thermoplastic binder with the composition paraffin – wax – oleic acid, taken in the ratios 82:15:3 in amounts 9.5 and 11.2 wt.%, were used for formation. The binder was removed by presintering blanks in air inside a KS 800 furnace at temperature 1200°C in an alumina charge. The final sintering of the samples was performed in a vacuum furnace with tungsten heaters, which was equipped with a high-temperature dilatometer, in a vacuum according to the following regime: heating in the temperature interval 20 – 1000°C at the rate 15 K/min and in the interval 1000 – 1900°C at the rate 5 K/min. The holding time at the final temperature ranged from 2 to 10 h.

Analysis of the kinetic sintering curves and structural characteristics of the ceramics shows that the shrinkage of the samples formed using ultrasound saturates earlier and passivates (Fig. 1). When the density reaches the same value, the samples formed with the use of ultrasound show smaller shrinkage (by 10 – 20%) than that of the control samples. The same density is reached in the later with longer sintering times.

The effect of ultrasonic treatment on the kinetics of sintering is most noticeable for samples cast from slips with a higher binder content. In this case, the densification stage is activated to a higher degree, which is expressed in a shift of

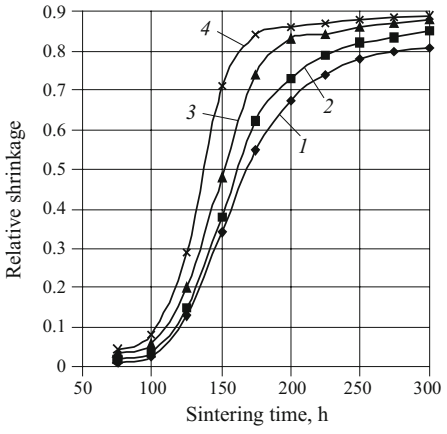

Fig. 1. Kinetics of densification of samples during sintering: *1* and *2*) without ultrasonic treatment, binder content 9.5 and 11.7%, respectively; *3* and *4*) ultrasonic power 3 kW, binder content 9.5 and 11.7%, respectively.

[1] Novosibirsk State Academy of Transportation by Water, Novosibirsk, Russia.

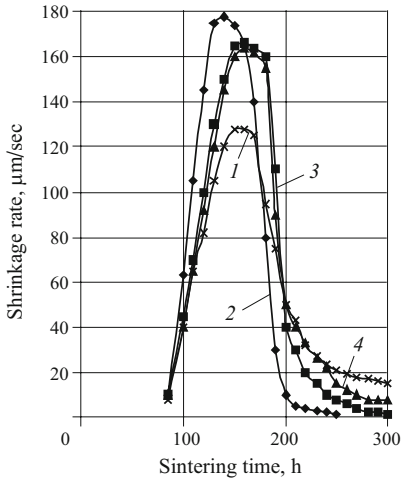

Fig. 2. Kinetics of densification of samples cast with the use of ultrasound: *1*, *2*, *3*, and *4*) ultrasonic power 3.0, 3.0, 3.5, and 4.0 kW, respectively.

the densification curve into the low-temperature region. Data on the kinetics of shrinkage also indicate more intense sintering of samples formed with the use of ultrasound (Fig. 2).

The effect of the ultrasonic power on the sinterability of all samples shows extremal behavior (Fig. 3). Evidently, this result is due to the decrease of the apparent density of the casting (Fig. 4) as a result of the ineffective compensation of the shrinkage during the formation of the structure in the course of casting [2]. The correlation between the ultrasonic power and the apparent density and maximum rate of shrinkage makes it possible to consider the latter parameters as criteria for optimizing the power used for ultrasonic treatment.

However, the change of the density of the casting is not the only factor affecting the kinetics of sintering. The increase of activity during the sintering of powders treated with ultrasound is probably also due to changes at the structural and substructural levels of the solid phase. This conclusion can be drawn on the basis of the results of an investigation of powders by electron microscopy and x-ray structural analysis. The change of the disperse composition of the powder during ultrasonic treatment is shown in Table 1. The effect of ultrasound is to change the granulometric composition and, for sufficient durations (> 15 min) and intensity (power not less than 3 kW), to change the sizes of the crystallites (Fig. 5).

Calculations of the activation energy of the sintering and recrystallization processes performed using the data on the time required to reach the same shrinkage and the same grain size as a function of the temperature showed that for samples treated with ultrasound as well as for the control samples these parameters are 960 ± 10 and 880 ± 10 kJ/mole. Close values of the activation energies for sintering and recrystallization processes show that these processes are based on the same mechanism — diffusion.

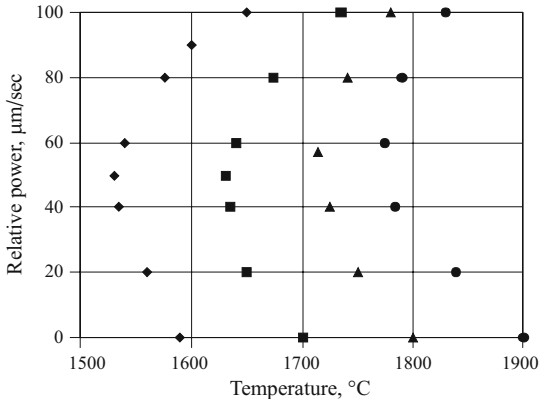

Fig. 3. Apparent density versus the ultrasonic power and sintering temperature. Apparent density of the ceramic (g/cm^3): ◆) 2.83, ■) 2.87, ▲) 2.89, ●) 2.90.

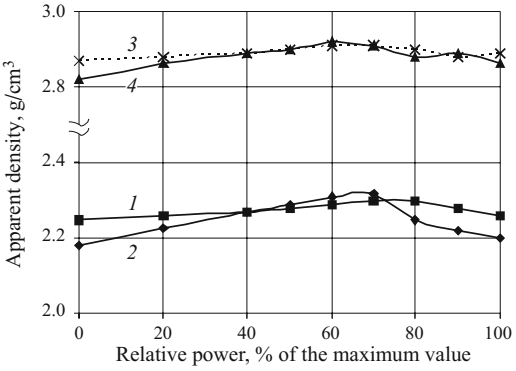

Fig. 4. Effect of the ultrasonic power on the density of the casting and the ceramic (sintering temperature 1850°C): *1* and *2*) casting from slip with binder content 9.5 and 11.2%, respectively; *3* and *4*) ceramic from slip with binder content 9.5 and 11.2%, respectively.

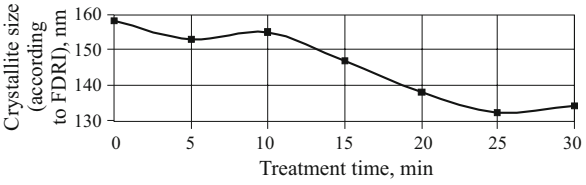

Fig. 5. Change of the size of the crystallites in the course of ultrasonic treatment.

TABLE 1.

Ultrasound power, kW	Granulometric parameters of the disperse phase	
	arithmetic-mean, μm	content of particles smaller than 1.5 μm, %
0	11.49	12.7
3.0	6.50	27.2
3.5	7.25	23.4
4.0	5.65	32.0

Consequently, looking at the experimental data from the standpoint of the phenomenological approach [3], it can be concluded that the similar form of the kinetic curve of sintering and the close values of the activation energies of the sintering and recrystallization processes in all samples show that the limiting mechanism of sintering of the ceramic sample formed with and without ultrasound is the same. The kinetics of active sintering of the samples at the average temperatures corresponds qualitatively to a threshold mechanism of flow of polycrystalline materials under the action of capillary forces. The absolute value of the rate of densification in this case can be estimated using the theory of locally nonuniform diffusion flow, in which slipping along grain boundaries and adjustment of their form by grain-boundary diffusion mass transfer play the main role [4]. At the same time the kinetics of sintering of the samples at high temperatures formally follows the Ivensen's phenomenology and is due to diffusion growth of subgrains. This is why the change of the rate of volume diffusion in the material during isothermal sintering is determined by the prehistory of the sample (initial density, dispersity of the solid phase) and the temperature of the sample.

In summary, the key changes associated with the homogenization of the material and the more compact packing of the powders at the formation stage as well as with the destruction and growth of defects in the particles and crystallites, which develop in powders under the action of ultrasound, intensify sintering and make it possible to lower the sintering temperature (50 – 150°C) and decrease the shrinkage (10 – 20%).

A decrease of shrinkage has a positive effect on good articles, and a decrease of the sintering temperature makes it possible to prolong the service life of the thermal equipment and decrease electricity consumption in the production of ceramic articles. The results of these studies confirm that ultrasound is useful at the formation stage and can be used to predict the sinterability of ceramic pastes activated by ultrasound at the formation stage.

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